

PERFORMANCE MONITORING OF A ZVI PRB CONSTRUCTED USING BIOPOLYMER SLURRY

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Background

A technology demonstration study using zero valent iron (ZVI) in a subsurface permeable reactive barrier (PRB) was recently initiated at the former Carswell AFB, Texas. This project was funded as a joint effort by the Air Force Center for Environmental Excellence, the Air Force Real Property Agency, and the Aeronautical Systems Center. The objective was to demonstrate the use of a ZVI PRB to abiotically degrade chlorinated ethenes, in particular trichloroethene (TCE), in groundwater. An innovative construction technique, the biopolymer slurry wall, was selected for construction of the ZVI PRB. This technique relies on a biodegradable biopolymer slurry (guar gum) to provide liquid shoring of the trench sidewalls.

In addition to TCE, the groundwater contaminants include cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC), and trace amounts of perchloroethene and trans-1,2-dichloroethene. Prior to design, a column study using the site groundwater was performed by Envirometal Technologies Inc. to determine the TCE, cis-1,2-DCE and VC degradation rates with pure ZVI and with a mixture of 50% ZVI/50% sand by dry weight. Because the column study was performed prior to selection of the construction technique, the column study did not evaluate the potential effect of the biopolymer slurry on the performance of the ZVI. Based on the literature, beyond increasing the period required for the PRB to achieve steady-state, the use of the biopolymer slurry was not expected to affect the ZVI performance (Focht, et al, 2001). A 50% ZVI/50% sand mixture at a design width of 2 feet was selected for the field installation. Without application of a safety factor to account for variation in the field conditions from the column study conditions, the column study predicted that a 2-foot wide PRB would achieve Federal maximum contaminant levels (MCLs).

The 1,126-foot long PRB was constructed between March and April of 2002. Three quarterly rounds of performance monitoring data have been collected. For brevity, this presentation focuses on the third quarter of performance monitoring data collected in December 2002. Comparison of the December 2002 data to the column study results has highlighted substantial differences between the cis-1,2-DCE and VC degradation observed in the laboratory and in the field. Three preliminary hypotheses have been developed to explain these differences: 1) occurrence of anaerobic biodegradation of TCE; 2) uncertainty in application of laboratory degradation rates to field conditions; and 3) inhibition of the sequential hydrogenolysis pathway under laboratory conditions but not under field conditions.

Methods

Performance monitoring wells are located upgradient of, within, and downgradient of the PRB to form 4 transects perpendicular to the PRB. In addition, a performance monitoring well is located adjacent to each end of the PRB to monitor for by-pass around the PRB. These transect and by-pass wells were sampled during each quarter.

Prior to purging the wells, depths to groundwater were measured. Groundwater samples were collected using the United State Environmental Protection Agency (EPA) low flow groundwater sampling method. Prior to sample collection, the field parameters dissolved oxygen, oxidation-reduction potential, temperature, pH, electrical conductivity, and turbidity were measured with a multi-meter and a flow-through cell. The samples were preserved, packed on ice, and shipped to a commercial laboratory for analysis. The samples were analyzed for selected volatile organic compounds by Method SW8260B, selected metals (calcium, iron, magnesium, manganese, potassium, and sodium) by Method SW6010B, anions (chloride, fluoride, nitrate and sulfate) by

Method SW9056, alkalinity by Method E310.1, reactive silica by Method SW6010B, total dissolved solids by Method E160.2, and dissolved and total organic carbon by Method E145.1.

To evaluate the potential for microbial activity to affect TCE degradation within or downgradient from the PRB, samples were collected for phospholipid fatty acid (PLFA) analysis in December 2002. A PLFA analysis provides estimates of the numbers and types of microbes present in the aquifer system. To perform the PLFA analysis, total lipids were extracted from the samples. The polar lipids were separated using column chromatography, derivatized to fatty acid methyl esters, and then analyzed using gas chromatography and mass spectrometry.

Results and Discussion

The June 2002 groundwater elevation data indicate that the groundwater flow has returned to pre-PRB construction patterns. There is no indication of mounding. Analytical results from and groundwater elevations in the by-pass monitoring wells indicate that groundwater is not preferentially flowing around the ends of the PRB. In addition, the groundwater surface is below the top of the reactive media, indicating no bypass over the ZVI as would be expected if the PRB were acting as a barrier to groundwater flow. The data indicate that use of the biopolymer slurry has not exerted a residual effect on the groundwater flow.

The results for TCE, cis-1,2-DCE and VC are presented in Table 1. The PRB appears to be very effective in the degradation of TCE. The influent TCE was degraded to less than 1 µg/L in Transect 1 and to below the detection limit (1 µg/L) in Transects 3 and 4. In Transect 2, the TCE was degraded to 10 µg/L, representing a removal efficiency of greater than 99 percent (%). These results are consistent with the column study.

Table 1. Results for TCE, cis-1,2-DCE and VC, December 2002

Transect	Analyte	Upgradient Concentration (µg/L)	In-PRB Concentration (µg/L)	Downgradient Concentration (µg/L)
1	TCE	1,400	1,000	0.81 F
	cis-1,2-DCE	350	350	8.2
	VC	25	16	ND
2	TCE	1,500	1,400	10
	cis-1,2-DCE	360	400	400
	VC	2.8	4.7	7.9
3	TCE	1,300	ND	ND
	cis-1,2-DCE	450	380	630
	VC	3.2 F	4.1 F	5
4	TCE	11	ND	ND
	cis-1,2-DCE	3.8	10	25
	VC	ND	0.78 F	1.2

F = estimated value

EPA Method 8260B

ND = not detected

The cis-1,2-DCE results varied substantially among the four transects. In Transect 1, the removal efficiency was greater than 97%, which is consistent with the column study results. In Transect 2, the 11% increase in the cis-1,2-DCE concentration between the upgradient well and the n-PRB well may be due to analytical variability or cis-1,2-DCE production, or a combination thereof. The cis-1,2-DCE concentration did not change between the in-PRB well and the downgradient well. In Transect 3, it appears that some removal of the cis-1,2-DCE did occur within the PRB. Between the in-PRB well and the downgradient well, however, the cis-1,2-DCE concentration increased by 65%. In Transect 4, the cis-1,2-DCE concentration increased by 6.6 times between the upgradient well and the downgradient well. This observed concentration increase may be partially due to the variability inherent to the analysis of volatile organic compounds at low concentrations. The majority of this increase occurred between the in-PRB well and the downgradient well. The cis-1,2-DCE results from Transects 2, 3, and 4 were not consistent with the column study. During the column study, no production of cis-1,2-DCE was observed. Production of cis-1,2-DCE along Transects 2, 3, and 4 is a substantial deviation from the column study results.

The VC data were not consistent with the column study results with the exception of Transect 1. In Transect 1, complete degradation of the influent VC was observed. This result is consistent with the column study. A small increase in the VC concentration was observed in Transect 2, although a substantial portion of this increase may

be due to the variability associated with the analysis of low concentrations. In Transects 3 and 4, there was no real change in VC concentration between the upgradient wells and the downgradient wells.

The PLFA data, presented in Table 2, were collected in order to assess the potential for microbial activity to affect degradation of the TCE within or downgradient from the PRB. In Transects 1, 3, and 4, the biomass concentration within the PRB was 2 to 5 times greater than that in the corresponding upgradient well. The biomass concentration increased substantially along each transect, from 2.8 times in Transect 2 to 29 times in Transect 1. By measuring the change in the fatty acid composition of the biomass, the PLFA analysis is able to identify shifts in the microbial community. The data indicate that the community shifted towards anaerobes along each transect. Not only did the absolute numbers of anaerobes increase, but their populations also tended to increase as a percentage of the total microbial community.

Table 2. PLFA Results

Transect	Upgradient Biomass (cells/mL)	In-PRB Biomass (cells/mL)	Downgradient Biomass (cells/mL)
1	13,800	74,600	403,000
2	44,000	18,500	123,000
3	6,910	23,400	79,500
4	44,900	90,700	188,000

The inorganic chemical data also support the development of an anaerobic microbial community. During the column study, flow through the ZVI media reduced the sulfate concentration by only 13%. For all transects, influent sulfate concentrations were reduced by greater than 98%. Except for Transect 1, the majority of the sulfate reduction occurred between the upgradient wells and the in-PRB wells. In general, the pH levels observed in the field were lower than those achieved in the column study. During the column study, pH's greater than 9.5 were measured within the column. In the field, one well within the PRB had a pH of 10.2 (Transect 4), and one downgradient well had a pH of 10 (Transect 1). The remaining in-PRB wells and downgradient wells had pH's between 6.82 and 7.15, slightly lower than the pH's in the upgradient wells. These latter pH's ranged from 6.7 to 7.15. Anaerobic microbial activity produces organic acids, which may have prevented the hydroxyls generated by corrosion of the ZVI by water from increasing the pH within the PRB.

To summarize the analytical results, the PRB has demonstrated very effective TCE degradation at a rate consistent with the column study. Some VC was degraded, and minor amounts of VC were produced in only one transect. Although Transect 1 exhibited excellent cis-1,2-DCE degradation, the other transects showed cis-1,2-DCE production. Because perchloroethene is non-detect in all wells except for a concentration of 1.5 µg/L in the upgradient well of Transect 2, the parent compound for the cis-1,2-DCE is likely TCE. The production of cis-1,2-DCE from TCE is not consistent with the results of the column study.

Three hypotheses were developed to explain the cis-1,2-DCE and VC results. First, the presence of the biopolymer slurry may have stimulated microbial activity, allowing the anaerobic biodegradation of TCE. Second, the factor used to adjust the column study degradation rates to account for differences between field conditions and column study conditions, such as temperature and pH, may not be reliable. Third, some aspect of the column study may have inhibited abiotic TCE degradation via the sequential hydrogenolysis pathway. The field conditions may allow for a fraction of the TCE to be degraded through this pathway.

As described above, the microbial community, the anaerobic portion in particular, may have been stimulated by the installation of the PRB. The use of the biopolymer slurry to install the PRB may be similar to the process of enhanced reductive dechlorination, which relies on the injection of readily bioavailable organic compounds to stimulate microbial activity and produce anaerobic conditions (Payne, et al, 2001). Microbial degradation of the easily degraded carbon sources decreases dissolved oxygen and nitrate concentrations, creating anaerobic conditions and promoting microbial growth. The guar gum used to make the biopolymer slurry is composed of long chains of galactose and mannose. Although initially the guar gum molecules were likely too large to be readily bioavailable, prior to capping the trench an enzyme was injected to reduce the length of the polysaccharides. It was necessary to break the polysaccharides into smaller molecules in order to restore the groundwater flow. This reduction in molecular size, however, could have rendered the polysaccharides bioavailable. This microbial food source combined with removal of the dissolved oxygen by ZVI corrosion may have generated, as shown by the data, sulfate-reducing conditions. TCE can be degraded under a wide range of anaerobic conditions, including sulfate-reducing conditions and methanogenic conditions (Boopathy and Peters, 2001; Castellanos, et al, 2002; Lutes, et al, 2002). Cis-1,2-DCE is one daughter product of anaerobic TCE degradation (Boopathy and Peters, 2001; Castellanos, et al, 2002). Recent research suggests that TCE-

degrading anaerobes are able to form colonies in ZVI media (Lampron, et al, 2001; Sfeir, et al., 2001). It is possible that some of the TCE degradation observed along the PRB transects may have been microbially-mediated, resulting in the production of cis-1,2-DCE. This cis-1,2-DCE accumulated in Transects 3 and 4, and potentially in Transect 2. Although it is possible for anaerobes to degrade TCE to ethene, cis-1,2-DCE degraders may not be ubiquitous at all sites (Castellanos et al, 2002).

The second hypothesis addresses the difference in conditions between the column study and the PRB. For example, the site groundwater is typically 5-7 degrees Celsius cooler than the groundwater temperature during the column study. A reduction in the groundwater temperature may affect the degradation rates of various chlorinated hydrocarbons differently (Bastiaens, et al, 2002). The pH observed in the field is substantially lower than the pH measured during the column study. Ebert, et al (2001) noted that some studies indicate that pH has a substantial effect on degradation rates, while other studies exhibit minimal pH effect. The column study did not include the use of biopolymer slurry. It seems unlikely that biopolymer slurry residue would have slowed cis-1,2-DCE and VC degradation without adversely affecting the TCE degradation, unless the residue allowed for preferential adsorption of TCE to the iron surface. TCE does have a higher organic carbon partition coefficient than cis-1,2-DCE and VC.

The third hypothesis concerns the abiotic degradation pathways. ZVI may degrade TCE directly to chloroacetylene by the β -elimination pathway (EPA, 1998). The chloroacetylene quickly degrades to acetylene and then ethene. Alternatively, the ZVI may degrade TCE to cis-1,2-DCE, VC, and then ethene via the sequential hydrogenolysis pathway (EPA, 1998). "Generally, less than 5%-10% of the initial TCE appears as chlorinated degradation products." (EPA, 1998, page 10) Because no generation of cis-1,2-DCE was observed during the column study, it was concluded that TCE degradation would occur solely through the β -elimination pathway. There are examples in which a ZVI treatment system has produced cis-1,2-DCE in the field (EPA, 2002; Remediation Technologies Development Forum (RTDF), 2003) and in the laboratory (Bastiaens, et al, 2002; EPA 1998; Kober, et al, date unknown). Perhaps some condition in the column study inhibited the sequential hydrogenolysis pathway, or some field condition promoted the sequential hydrogenolysis pathway.

Future research on the role of microbes in the degradation of TCE subsequent to PRB installation via the biopolymer slurry wall technique is recommended. In addition, it is recommended that research be performed to refine the application of column study data to the design of full-scale PRBs in order to account for the differences between laboratory conditions and field conditions.

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